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Theory of Multi-Coordination Centered Catalyst

A Proposed Mechanism of Stereoregular Polymerization

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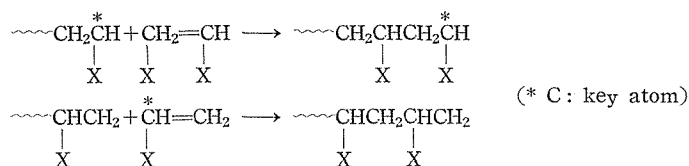
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Stereoregular polymerizations of various monomers including α -olefins, vinyl compounds, diolefins, aldehydes and alkylene oxides have been known. In this article, the theory of "Multi-Coordination Centered Catalyst" is proposed for the mechanism of stereoregular ionic polymerization. It is emphasized that the catalysts having two coordination centers would be favorable for stereoregulation: one center is the counter ion of the growing polymer end and the other center is linked with the counter ion by halfbonding, oxide linkage or ion-molecule linking through coordination. In vinyl polymerization, the first center (counter ion center) is paired with growing polymer end by forming ion pair and the second center restricts free rotation in chain end by coordination with two adjacent polar substituents. In the polymerizations of α -olefin, aldehyde and alkylene oxide, the key atom is present in the monomer side and the coordination centers link with the monomer to regulate the configuration of the incoming monomer molecule, where stereoregulation can be effectuated by the ligand of the catalyst. The cis-addition of diolefin polymerization can be explained by 1,4-coordination of the diolefin monomer with catalyst.

INTRODUCTION

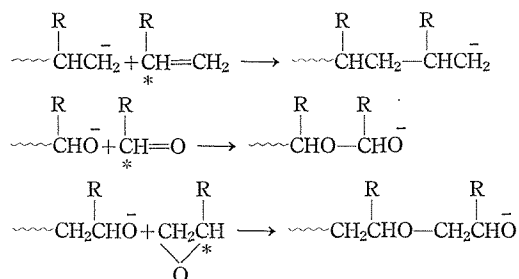
Since Natta's discovery of isotactic poly(olefin), the stereoregular polymerization afforded a splendid field for the polymer chemists not only in poly(α -olefin) but also in polymer of polar compounds such as vinyl compounds, aldehydes, alkylene oxides. Despite tremendous works by a number of chemists the mechanism of stereoregulation is not yet entirely elucidated. Here an attempt to explain the mechanism is made in terms of some hypothetical consideration.

Prior to discussion it may be necessary to mention the problem of the position at which the stereoregulation takes place or of the key atom designating polymer structure, although it is not a true asymmetric atom in many cases. In the stereoregular polymerization there are two types of polymerization; in one case the key atom is present in growing chain end and in the other case it is in monomer as illustrated below.



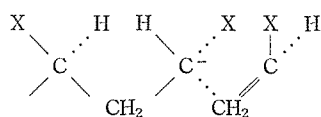
* 古川淳二

In vinyl polymerizations, both radical and ionic, the addition takes place generally at the β -carbon of monomer and consequently the problem is how the configuration of the α -carbon of polymer end would be settled either to *d*- or to *l*-form. On the other hand coordinated anionic polymerization of α -olefin by Ziegler catalyst as well as that of aldehyde or propylene oxide may proceed through addition at the α -position of monomer, the key atom being the α -carbon of monomer.

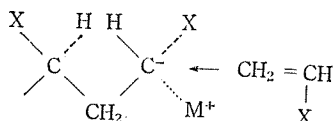


Stereogular polymerization is conducted in general by ionic catalyst and rarely by radical catalyst, but the latter catalyst results in the formation of only incomplete syndiotactic polymer even at an extremely low temperature. Most of excellent catalysts seen to be found in anionic but not cationic polymerization. However, it has recently been reported that isotactic polyvinylether can be prepared by cationic polymerization with use of special catalyst¹¹.

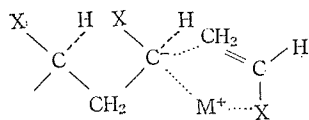
It is said that stereoregulation requires special conditions, such as use of non-polar solvent²⁾, low-temperature polymerization³⁾ and use of associated catalyst⁴⁾ or solid catalyst. Several theories have been proposed for the explanation of above mechanism but most of them seem to be valid only for limited cases. A theory proposed here involves the general principle of mechanism for stereoregulation of every kind, which I call the theory of multi-coordination centers. The ionic polymerizations are classified into the following four types (Fig. 1):



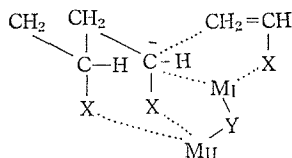
(1) Free ion polymerization



(2) Paired ion polymerization



(3) Coordinated ionic polymerization



(4) Multi-center coordinated ionic polymerization

Fig. 1.

Each type of polymerization may possibly exist, where by more or less stereoregulation may be expected, and the multi-coordination centered polymerization is

considered to be the most effective. In the following sections several examples will be explained according to the above theory.

If the addition takes place on β -position of monomer, the key atom exists on the chain end of growing polymer. In the case of free ionic addition the stereoregulation seems to be possible only at extremely low temperatures at which free rotations around main chain are restricted so as to maintain the most stable conformation of each carbon atom along the main chain.

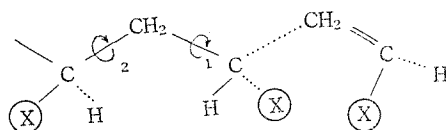


Fig. 2.

Here the trans conformation at each carbon atom may be more plausible from the viewpoint of stereochemistry and this conformation may make it possible to form the planar zigzag structure of polymer at low temperatures, wherein the two polar substituents, which are repulsive to each other, are held at their largest mutual separation, *i.e.*, syndiotactic structure (Fig. 2). Sometimes⁵⁾ the repulsion between the substituent of monomer and that of polymer chain is taken into account, but such an effect seems rather less significant because the distance between chain end and monomer is in general longer than the chemically bonded carbon-carbon distance. Moreover, the consideration on the effect arising from monomer substituent does not lead to any different conclusion from the above discussion.

Fordham *et al.*,⁶⁾ estimated the repulsion energy of polar substituent like chlorine roughly at 1 kcal./mole and concluded the predominant formation of the syndiotactic structure in the polymerization at low temperatures. In fact, experiments in free ion polymerization showed the formation of syndiotactic polymer without any exception. From these considerations it is said that there is no significant difference between radical polymerization and free ion polymerization. In the polymerization in non-polar solvent the growing polymer ion is accompanied by counter ion, which is supposed to affect more or less the conformation of the key atom rather through interaction between the substituent X in chain end and the ligand Z of counter ion as is illustrated in Fig. 3.

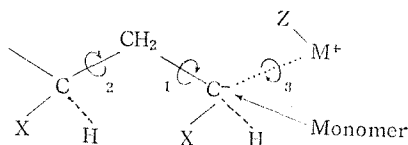


Fig. 3.

But the rotations around the bond 1 and 3, both of which can rotate independently, seem to be too free to fix X and Z in definite position, and hence stereoregulation is less effective except at low temperatures.

Theory of Multi-Coordination Centered Catalyst

The coordinated polymerization mechanism was proposed by Natta *et al.*⁷ in order to explain isotactic polymerization of α -olefin by Ziegler-Natta catalyst and we adopted it to the anionic polymerization of acetaldehyde by organometallic catalyst⁸. This concept is based on the assumption that the polymerization proceeds by the attack of polymer end onto monomer which is coordinated on the catalyst ion as illustrated in Figs. 4 and 5.

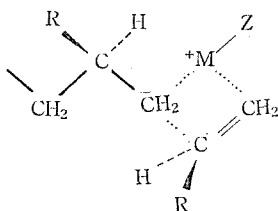


Fig. 4.

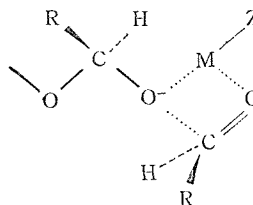


Fig. 5.

It is to be noticed that in both cases the key atom is not in polymer end but in monomer, because it is the case of α -addition in monomer, and therefore the interaction with respect to substituent relates not only to the substituent in polymer but also to the ligand attached to the catalyst. The ring formation at transition state may make it easy to form a fixed arrangement favorable for regular structure, but such a ring involving three transitory bondings may be so unstable that the effective stereoregulation cannot be expected.

Multi-coordination center hypothesis has been proposed in order to explain more efficient stereoregulation, which will be discussed with many examples.

I. MULTI-CENTER COORDINATED POLYMERIZATION WHERE A KEY ATOM EXISTS IN THE POLYMER END

The theory is based on the assumption that the catalyst possesses more than one coordination center, one of which is linked to the two polar substituents near polymer end and the other center is paired with chain end. By this way there is formed a comparatively rigid ring structure as shown in Fig. 6. If substituents are so bulky that they do not permit planar zigzag structure, the spiral may be taken. In the latter case multicentered catalyst is coordinated by adjacent polar groups in the same phase near chain end to give rise to isotactic polymerization as shown in Fig. 7.

In case of α -addition in monomer the polar groups in monomer are coordinated onto two coordination centers of catalyst. Here a rigid ring structure containing

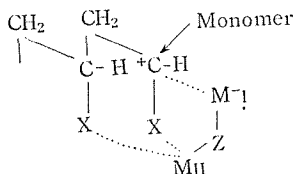


Fig. 6.

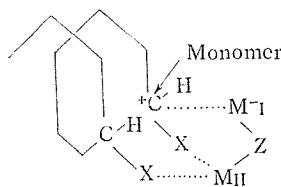


Fig. 7.

two transitory bonds is formed which may make possible the stereoregulation of key atom in monomer by the interaction between the substituent R of monomer and the ligand Y of catalyst. The rough illustration is shown in Fig. 7, whose detailed discussion will be made in the subsequent chapter.

I-1. Stereoregular Cationic Polymerization of Vinyl Ethers

In the polymerization of vinyl ethers, oxygen in ether group is capable of coordinating. If two adjacent ether groups near chain end are linked to the second catalyst center the isotactic polymer may be expected by the attack of the coordinating monomer, which adds to chain end entering from the opposite side of polymer chain (Fig. 8).

According to this there should be a complex catalyst which possesses at least two coordination centers.

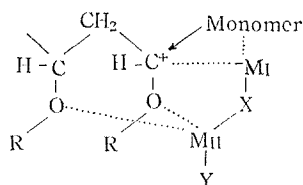
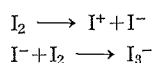
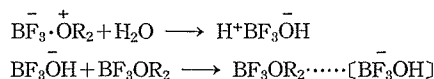


Fig. 8

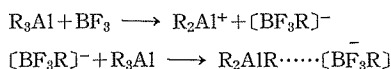
In anionic polymerization organometallic catalyst is expected to form a complex compound of this type by oxygen linkage or half-bonding. On the contrary, in cationic polymerization there had not been considered the coordination. But if the center atom in counter anion is linked with considerably electronegative ligand such as halogen or oxygen, positive formal charge on center atom may make further coordination possible. For example, iodine molecule is known to be dissociated into triiodoanion such that



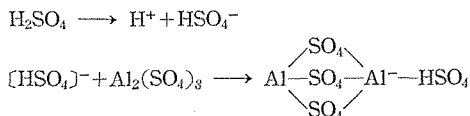
Stereoregulation in cationic polymerization of vinyl ether is known when it is conducted in conditions favoring association of catalyst, *i.e.*, at low temperatures and in non-polar solvents. Boron fluoride etherate possibly exists in associated form in suitable condition. For instance,



Many excellent catalysts are recently found in combined system of sulfuric acid—metal sulfate⁹⁾ or metal alkyl—Lewis acid¹⁰⁾. These are so active in stereoregulation that isotactic poly(vinyl ether) is produced even at room temperature. It is in contrast to the polymerization with simple Lewis acid like $\text{BF}_3 \cdot \text{CR}_2$, wherein it must be conducted at very low temperature. These systems seem to form complex anion more easily through the following mechanism:



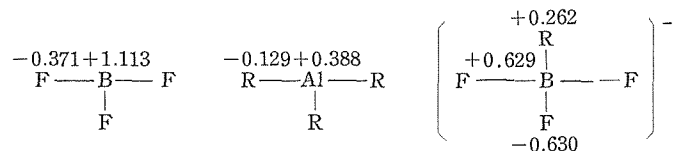
and



The complex ion resulting from combination of anion with basic molecule may act as the so-called multi-center coordination catalyst. Here, the large positive charge density of center atom in anion is expected and it may cause further coordination of another molecule. Charge density of atom may be estimated from electronegativity. For instance, in boron trifluoride the ionic character δ of B-F bond is estimated at 0.65 from their electronegativities X_F and X_B , respectively, according to Pauling's expression,

$$\delta = 1 - \exp\left\{-\frac{1}{4}(X_F - X_B)^2\right\}.$$

And hence total charge on boron will roughly be equal to 1.95, the sum of ionic character, but more correct value is to be calculated by considering feed-back effect of other boron-fluorine bonds¹¹⁾. The following are examples of corrected charge density.



From these, alkylboronfluoride anion $[\text{RBF}_3]^-$ is known to be still acidic even toward trialkylaluminum, since positive charge density on boron of the former is larger than that on aluminum in trialkylaluminum. Therefore, the difference between both charge densities may be taken as the measure of the rough tendency toward further coordination. According to this concept the charge differences are calculated for the catalysts proposed by Nakano *et al.*¹⁰⁾, and we found the good parallelity of stereoregulating ability of combined catalyst to the charge difference between corresponding components as summarized in Table 1.

This table seems to suggest that the combination of acidic component of Lewis acid type and metal alkyl would form a complex anion and induce the stereoregular polymerization. Catalysts consisting of one component are poor in ability to form complex, except alkyl metal sesquihalide, the latter of which was known as a catalyst of the medium regulating ability. It gave both crystalline and atactic polymers perhaps with complex active species and simple one, which existed simultaneously. The content of crystalline polymer may depend upon the content ratio as well as activity ratio of both catalyst species and may be affected by temperature, solvent and other condition. The catalyst containing metal-oxygen linkage may afford the so-called multi-center complex of excellent ability but is used in a solid form on account of poor solubility.

In this sense the concept of multi-center coordination involves adsorption on solid catalyst. In fact, these were known many excellent catalysts in solid catalyst systems.

Table 1. Charge density and stereoregulating property

No.	Catalyst system	R.A.	Anion	e_A	Molecule	e_M	$e_A - e_M$
1	$R_3Al + BF_3$	††	RBF_3^-	+0.629	R_3Al	+0.388	+0.241
2	$R_3Al + VCl_4$	††	$RVC l_4^-$	+0.454	R_3Al	+0.388	+0.066
3	$R_3Al + TiCl_4$	††	$RTiCl_4^-$	+0.521	R_3Al	+0.388	+0.133
4	$R_3Al + SnCl_4$	+	$RSnCl_4^-$	+0.273	R_3Al	+0.388	-0.115
5	$R_3Al + SbCl_5$	+	$RSbCl_5^-$	+0.265	R_3Al	+0.388	-0.123
6	$Et_2AlCl + H_2O$	+	$Et_2ClAlOH^-$	+0.384	Et_2AlCl	+0.506	-0.122
7	$EtAlCl_2 + H_2O$	+	$EtCl_2AlOH^-$	+0.474	$EtAlCl_2$	+0.624	-0.146
8	$BF_3 \cdot OR_2 + H_2O$	+	F_3BOH^-	+0.746	BF_3OR_2	+0.870	-0.136
9	$CH_3TiCl_3 + H_2O$	-	$CH_3Cl_3TiOH^-$	+0.579	CH_3TiCl_3	+0.722	-0.143
10	$TiCl_4 + H_2O$	-	Cl_4TiOH^-	+0.660	$TiCl_4$	+0.820	-0.160
11	$AlCl_3 + H_2O$	-	Cl_3AlOH^-	+0.572	$AlCl_3$	+0.741	-0.169
12	$VCl_4 + H_2O$	-	Cl_4VOH^-	+0.587	VCl_4	+0.761	-0.174
13	$SnCl_4 + H_2O$	-	Cl_4SnOH^-	+0.219	$SnCl_4$	+0.402	-0.183
14	$VOCl_3 + H_2O$	-	$HOVOCl_3^-$	+0.786	$VOCl_3$	+0.971	-0.186

Table 2. Complexs having oxygen linkage.

No.	Catalyst system	R.A.	Most probable structure
1.	$Al_2(SO_4)_3 - H_2SO_4$	††	$ \begin{array}{c} \begin{array}{ccccccc} & O & & O & & O & \\ & & & & & & \\ -O & -Al- & O- & S- & O- & Al- & O- \\ & & & & & & \\ & & & O & & & \\ & & & & & & \\ & & & O=S=O & & & \\ & & & & & & \\ & & & OH & & & \end{array} \end{array} $
2.	$Et_3Al - H_2SO_4$	††	$ \begin{array}{l} Et_3Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + C_2H_6 \uparrow \\ H_2SO_4 \\ \longrightarrow \text{The Same complex as in No. 1.} \end{array} $
3.	$CrO_3 - H_2O$	††	$ \begin{array}{c} \begin{array}{ccccc} & O & & O & OH \\ & & & & / \\ -O & -Cr- & O- & Cr- & O- \\ & & & & \\ & O & & O & \end{array} \end{array} $
4.	$CrO_2Cl_2 - H_2O$	††	$ \begin{array}{c} \begin{array}{ccccc} OH & OH & Cl & & \\ & & & & \\ O=Cr- & O- & Cr=O & & \\ & & & & \\ Cl & & Cl & & \end{array} \end{array} $
5.	$TiCl_2(OR)_2 - H_2O$	††	$ \begin{array}{c} \begin{array}{c} TiCl_2(OR)_2 \\ H_2O \end{array} \left. \vphantom{\begin{array}{c} TiCl_2(OR)_2 \\ H_2O \end{array}} \right\} \longrightarrow \begin{array}{c} \begin{array}{ccccc} Cl & & Cl & & \\ & & & & \\ -O-Ti- & O- & Ti- & O- & \\ & & & & \\ Cl & & Cl & & \end{array} \\ \\ \begin{array}{c} H_2O \\ \longrightarrow \end{array} \begin{array}{c} \begin{array}{ccccc} Cl & & Cl & OH & \\ & & & / & \\ -O-Ti- & O- & Ti- & O- & \\ & & & & \\ Cl & & Cl & & \end{array} \end{array} \end{array} $

Table 2 is made using Nakano's result¹⁰⁾, in which the possible structures assumed by us are listed additionally. These catalysts are formed by the combination of anion and neutral molecule through oxide linkage and therefore can be regarded as so-called multi-coordination catalysts. Stereoregulation is sometimes accounted for by regular adsorption of monomer¹²⁾ on solid catalyst but the multi-center concept does not always require solid state of catalyst and does not mean the regular adsorption of monomers on solid catalyst but coordination of adjacent polar groups near end in polymer chain onto multi-centered catalyst.

I-2. Anionic Polymerization of Acrylic Compounds

Polymer of acrylic compound has carbonyl as a functional group, on which multi-center coordination may be possible by complex catalyst as is illustrated in Fig. 9. Spiral structure is more probable from steric requirement (Fig. 10).

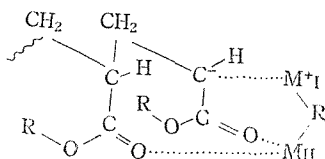


Fig. 9.

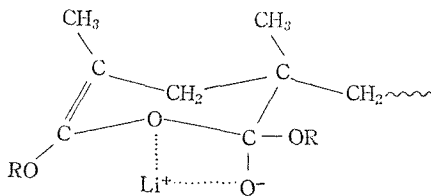
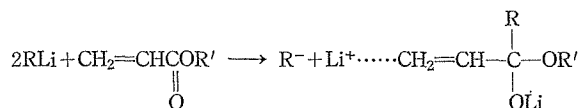
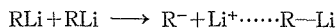
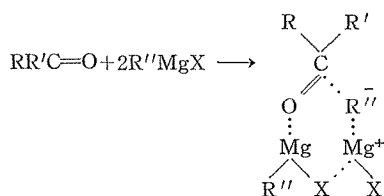


Fig. 10.

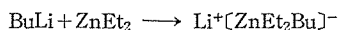
These structures are both favorable for the formation of isotactic polymer. Essentially Fig. 9 is the same as the model of Cram¹³⁾, who supposed the enolate ring structure paired with lithium cation (Fig. 10). On the other hand a spiral structure was proposed by Glusker¹⁴⁾. Both authors seem to try to explain the stereoregulation by lithium cation, and in these cases the associated catalyst seems to be more favorable for suitable arrangement of monomer, because simple lithium cation has not so large ability to coordinate three atoms. Moreover the distance between lithium cation and key atom seems to be too long to contribute to stereoregulation. In fact, alkyllithium was reported to afford more crystalline polystyrene as it was used in higher concentration or in more associated state¹⁵⁾. Lithium cation may afford crystalline polymer when it is in associated form or complex form as



The addition of Grignard's reagent to carbonyl compound is known to proceed through a cyclic transition state, which consists of two moles of reagent. The transition structure is very similar to the above complex.



Many complex type catalysts consisting of two kinds of metal alkyls or metals were investigated whereby the so-called "At-Komplex" is formed, e.g.,



Many suitable groups of catalyst for methacrylate polymerization were found which are listed in Table 3 and Table 4. Results are rather complicated but Table 3 may lead to some conclusion that isotactic-forming ability increases as p-character of the cation becomes larger in the order of $\text{Na} < \text{Li} < \text{Ba} < \text{Sr}$ and as the anion complex involves more hydrogens instead of alkyl groups in the order of $\text{R}_n < \text{HR}_{n-1} < \text{H}_m\text{R}_{n-m} < \text{H}_n$. This fact seems to correlate to the complex formation by half bonding such as

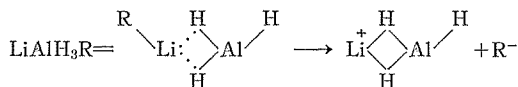


Table 3.

Type of crystalline poly(methyl methacrylate)	Combination of metal and alkyl metal and At-Complex resulted
Isotactic	$\text{LiAlH}_4 + \text{Et}_2\text{Zn} \longrightarrow \text{LiAlH}_{4-n}\text{R}_n + \text{Zn} + \text{RH}$
	$\text{LiAlH}_4 + \begin{cases} \text{Et}_2\text{Cd} \\ \text{Et}_3\text{Al} \\ \text{Bu}_3\text{B} \\ \text{Bu}_2\text{Hg} \end{cases}$
	$\text{Ba} + \text{Et}_2\text{Zn} \longrightarrow \text{BaZnEt}_4 + \text{Zn}$
	$\text{Sr} + \text{Et}_2\text{Zn} \longrightarrow \text{SrZnEt}_4 + \text{Zn}$
Stereoblock	$\text{Li} + \text{Et}_2\text{Zn} \longrightarrow \text{LiZnEt}_3 + \text{Zn}$
	$\text{Na} + \text{Et}_2\text{Zn} \longrightarrow \text{NaZnEt}_3 + \text{Zn}$
	$\text{LiH} + \text{Et}_2\text{Zn} \longrightarrow \text{LiZnHEt}_2$
	$\text{NaH} + \text{Et}_2\text{Zn} \longrightarrow \text{NaZnHEt}_2$
	$\text{LiH} + \text{Et}_3\text{Al} \longrightarrow \text{LiAlHEt}_3$
	$\text{NaH} + \text{Et}_2\text{Cd} \longrightarrow \text{NaCdHEt}_2$

Table 4.

Anion*	Cation			
	Sr	Ba	Li	Na
MH_n			LiAlH_4	
$\text{MH}_m\text{R}_{n-m}$			LiAlH_3R LiAlH_2R_2	
MHR_{n-1}			LiAlHEt_3 LiZnHEt_2	NaZnHEt_2 NaCdHEt_2
MR_n	SrZnEt_4	BaZnEt_4	LiZnEt_3	NaAlEt_4 NaZnEt_3
	Isotactic		Stereoblock	Atactic

* M means metal.

wherein half bonding can exist when one cationic metal is divalent and of larger p-character like Li, Ba, Sr or Ca and the bridging atom is hydrogen or alkyl of small size like methyl. Since alkyl anion is more stable than hydride anion, the replacement of hydrogen by alkyl may enhance the tendency of the alkyl anion formation but it makes the bridge formation more difficult. At least two hydrogen atoms must be left unreplaced for the bridge formation.

The ease of the complex counter ion formation for several anionic catalysts has been calculated in the same manner as adopted for cationic catalyst systems. It is assumed that in each binary catalyst system, one component is the anionic source and that the counter cation of the anionic species formed from the anionic source is coordinated to the other component to give the multi-center cation. In Table 5, the calculation results are compared with the stereoregulating abilities of these catalytic systems observed for anionic polymerization of butyl acrylate. Here also the concept of multi-centered coordination seems to be satisfactory. Investigation on other monomers related to methyl methacrylate as follows indicates the effects of groups attached to key atom¹⁶⁾.

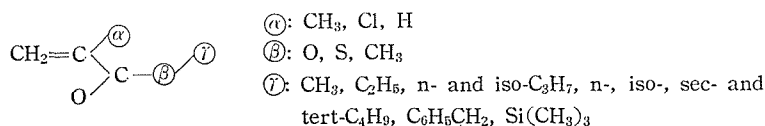
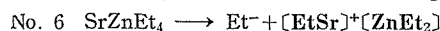
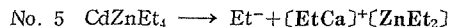
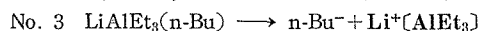
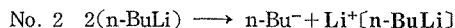
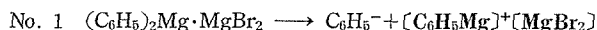


Table 5. Charge density in ion—molecule complex.

No.	Catalyst system	R.A.	Cation	e_O	Molecule	e_M	$e_O - e_M$
1	C ₆ H ₅ MgBr	+	R-Mg ⁺	+0.99	MgBr ₂	+0.6963	0.2937
2	n-BuLi	+	Li ⁺	+1.00	R-Li	+0.4200	0.5800
3	Et ₃ Al-n-BuLi	††	Li ⁺	+1.00	R ₃ Al	+0.3882	0.6118
4	Et ₂ Cd-n-BuLi	††	Li ⁺	+1.00	R ₂ Cd	+0.2222	0.7778
5	Ca-ZnEt ₄	‡‡‡	R-Ca ⁺	+1.07	R ₂ Zn	+0.2667	0.8033
6	Sr-ZnEt ₄	‡‡‡	R-Sr ⁺	+1.07	R ₂ Zn	+0.2667	0.8033

Assumed active species (bold-faced) for each catalyst system :



The conclusions are such that :

1. When α is equal to H, *i. e.*, acrylate *etc.*, bulky γ group such as iso-C₃H₇, sec- and tert-C₄H₉ seems to favor stereoregulation. And this fact suggests that the bulky group would control the free rotation in main chain and would effectuate the rigid regular conformation in main chain as far as bulkiness does not go over the limit value at which steric hindrance becomes too large.

2. Stereoregulation tends to decrease as α group becomes bulkier and α -methyl derivative affords crystalline polymer only when γ is methyl, and α -chlorine derivative does so when γ is sec-butyl and β is sulfur.

3. Thiol esters, when β is sulfur, are stereoregulated more easily and this property seems to be attributed to the enhancement of coordination at carbonyl by sulfur atom of less electronegativity.

II. STEREOREGULATION OF THE KEY ATOM PRESENTING IN MONOMER

This type of stereoregulation may be expected in anionic polymerization of aldehyde and alkylene oxide. Ziegler-Natta's coordinated anionic polymerization is also of this kind in a wide sense. Since the key atom is present in monomer, stereoregulation may be conducted by interaction of the substituent of monomer with the ligand on catalyst or with the substituent of polymer end. According to multi-center coordination concept the following models seem to be probable (Figs. 11 and 12).

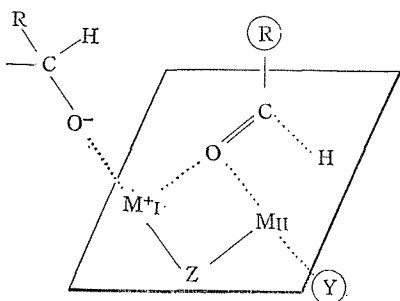


Fig. 11.

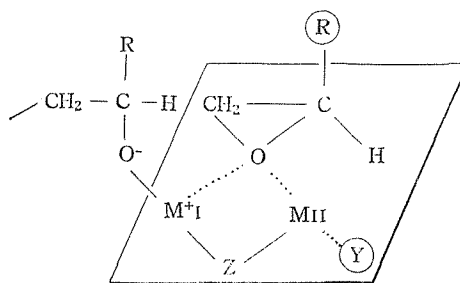


Fig. 12.

A monomer coordinating to two centers of catalyst maintains the definite position against polymer end and catalyst. Hence the substituent R possesses the characteristic position against that of ligand Y and this may induce the successive addition of the same configurations, and results in the formation of the isotactic structure. On the contrary, possible structures rendered by coordination of simple counter ion seem to be less stable and therefore less probable, because free rotation in coordination bond is not prohibited completely (Figs. 13 and 14). Even if there is assumed a ring structure, consisting of monomer, polymer and catalyst it may not be enough stable, because it contains three transitory bonds (Figs. 15 and 16).

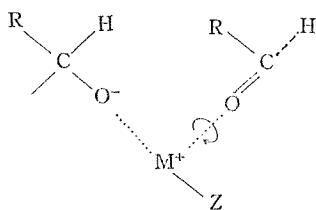


Fig. 13

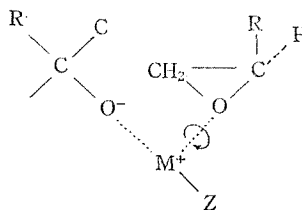


Fig. 14.

Theory of Multi-Coordination Centered Catalyst

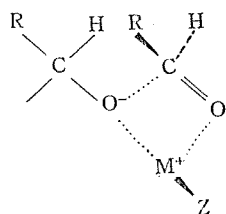


Fig. 15.

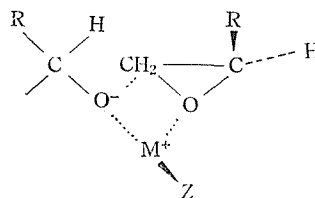
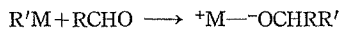


Fig. 16.

In the case of alkylene oxide, the stereoregulation is effected by selective coordination of *d*- or *l*-isomer on catalyst, depending on the nature of ligand Z.

II-1. Anionic Polymerization of Acetaldehyde

Acetaldehyde and related aldehydes were found to polymerize by use of metal alkyl¹⁷⁾ and aluminum oxide¹⁸⁾ as catalyst, the former catalyst gave crystalline polymer and the latter catalyst amorphous¹⁸⁾ one. Lewis acid type catalyst was also reported to afford atactic polymer of acetaldehyde¹⁹⁾. Metal alkyl may convert into metal alkoxide by the reaction with aldehyde prior to polymerization.



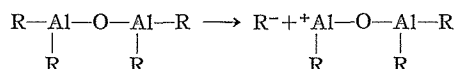
In fact, metal alkoxides prepared from various alcohols were found to have similar

Table 6.

Catalyst	Possible structure	Stereoregularity
Metal alkyl (reacted with aldehyde)	$ \begin{array}{c} R \\ \\ R-Al-O-Al-R \\ \quad \\ OR \quad OR \\ \\ R \end{array} $	Isotactic and atactic
Metal alkoxide	$ \begin{array}{c} R \\ \\ RO-Al-O-Al-OR \\ \quad \\ OR \quad OR \\ \\ R \end{array} $	Isotactic and atactic
Partly-hydrolyzed metal alkyl	$ \begin{array}{c} R-Al-O-Al-R \\ \quad \\ R \quad R \end{array} $	Stereoblock
Partly-hydrolyzed metal alkoxide	$ \begin{array}{c} RO-Al-O-Al-OR \\ \quad \\ OR \quad OR \end{array} $	Stereoblock
Metal oxide	$ \begin{array}{c} -O-Al-O-Al-O- \\ \quad \\ O \quad O \end{array} $	Atactic

activity. Furthermore, metal alkyl and metal alkoxide are found to be activated by partial hydrolysis, whereby alkyl metal oxide may be actual catalyst. It is interesting that partly-hydrolyzed catalyst can afford stereoblock polymer. Table 6 shows the various catalyst and their possible structure.

From Table 6 it is concluded that active catalyst is used to have a linkage of metal-oxygen, which seems to be favorable for formation of multicenter catalyst, *e. g.*,



Complex cation of $\text{RAlO}_{1/2}-\text{R}_2\text{AlO}_{1/2}$ structure may thus be formed.

Alumina, on the other hand, does not afford crystalline polymer but atactic on despite its metal-oxygen linked structure.

The lack of stereoregulating ability of alumina is somewhat queer, but there seems to be the possibility of cationic polymerization because aluminum oxide acts often as Lewis acid. Replacement of alkyl groups by aluminum-oxygen linkage may make the compound more acidic because of the increase of positive charge density on aluminum atom as is shown in Table 7.

Table 7.

R_3Al	+0.3882	R_2Zn	+0.2667
$\text{R}_2-\text{Al}-\text{O}-\text{Al}-\text{R}_2$	+0.5385	$\text{R}-\text{Zn}-\text{O}-\text{Zn}-\text{R}$	+0.4538
$\begin{array}{c} \text{R}-\text{Al}-\text{O}-\text{Al}-\text{R} \\ \quad \\ \text{OR} \quad \text{OR} \end{array}$	+0.7838	$-\text{O}-\text{Zn}-\text{O}-$	+0.6824
$\begin{array}{c} -\text{O}-\text{Al}-\text{O}-\text{Al}-\text{O}- \\ \quad \\ \text{O} \quad \text{O} \end{array}$	+0.9219	$\text{RO}-\text{Zn}-\text{O}-\text{Zn}-\text{OR}$	+0.7616
$\begin{array}{c} \text{RO}-\text{Al}-\text{O}-\text{Al}-\text{OR} \\ \quad \\ \text{OR} \quad \text{OR} \end{array}$	+1.0186	$\text{RO}-\text{Zn}-\text{OR}$	+0.8196
$\begin{array}{c} \text{RO}-\text{Al}-\text{OR} \\ \\ \text{OR} \end{array}$	+1.0517		

II-2. Coordinate Anionic Polymerization of Propylene Oxide

Polymerization of alkylene oxide is very similar to that of acetaldehyde. They are polymerized by common catalysts. It was found that diethylzinc was much enhanced in activity when it was treated with an almost equimolar amount of water. Dialkylzinc oxide or its homologue may be the actual catalyst which affords polymer containing less soluble crystalline portion, although its content does not exceed thirty percent. Two types of active species may be present, which are assumed to be the simple zinc alkoxide and the complex alkylzinc oxide; the former affords atactic polymer and the latter crystalline one. Coordinate anionic mechanism is assumed from the finding that the polymer contains the alkoxyl

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fragment arising from the catalyst. The catalyst is made from dibutylzinc treated with alcohol, whereby 9,10-anthracene dimethylol is used and detected by ultraviolet analysis. Moreover, optically active poly(propylene oxide) was obtained by asymmetric induction from *dl*-monomer, when the diethylzinc activated with (+) borneol or (–) menthol is used as the catalyst (Table 8).

Table 8. Asymmetric induction in polymerization of propylene oxide.

Activator	Solvent for polymer	η_{sp}/C	$[\alpha]_D$ of polymer	
			in benzene	in chloroform
(+) Borneol	Toluene	5.63	–5.9°	+7.4°
(+) Borneol	Hexane	3.30	–4.9°	+6.1°
(+) Borneol	Benzene	3.65	–3.7°	+2.5°
(–) Menthol	Benzene	0.59	–3.6°	+4.2°

Polymerization: Propylene oxide, 0.5 mole; solvent, 30–35 ml.; at 80°C.; at conversion, 17–30%.

Catalyst: Diethylzinc, 0.025 mole; alcohol, 0.05 mole.

Polymer: Crystalline fraction, ca. 10% except for (–) menthol (2.7%).

Optical rotation: Measured in 1–3% solutions at 10–15°C.

Here, the optical rotation of polymer is proved to arise not from alcoholic fragment attached to polymer but from polymer configuration, because rotation is too large to be regarded as the fragment effect and besides inversion of rotation is found in different solvents, in agreement with the results reported by Price²¹, who prepared *l*-polymer from *l*-propylene oxide.

It is still a question how asymmetric induction takes place, either direct induction by catalyst ligand to polymer chain or indirect induction through chain. In the latter case asymmetric induction may be caused by alkoxide anion but further regulation is caused by the successive induction by the penultimate unit. However, the neighboring asymmetric centers seem to be too far apart from each

Table 9. Crystalline fraction in polypropylene oxide prepared by the system of dibutylzinc and alcohols.

(Monomer, 0.05 mole; solvent, 3.5 ml. toluene; catalyst, 0.0023 mole Bu_2Zn ; cocatalyst, 0.0046 mole alcohol; polymerization, room temp.)

Alcohol	Polymer yield (%)	Crystalline fraction (%)
CH_3OH	68	9.2
$\text{C}_2\text{H}_5\text{OH}$	51	5.3
<i>n</i> - $\text{C}_3\text{H}_7\text{OH}$	85	2.8
<i>iso</i> - $\text{C}_3\text{H}_7\text{OH}$	trace	—
<i>n</i> - $\text{C}_4\text{H}_9\text{OH}$	93	1.6
<i>iso</i> - $\text{C}_4\text{H}_9\text{OH}$	33	15.1
<i>sec</i> - $\text{C}_4\text{H}_9\text{OH}$	trace	—
<i>tert</i> - $\text{C}_4\text{H}_9\text{OH}$	nil	—

other to control the effective induction. According to the coordination theory the direct effect of catalyst ligand on the conformation of monomer in each propagation step seems to be more influential. In the experiment using various alcoholic activators, not only catalytic activity but also crystalline fraction was affected as shown in Table 9.

Here it is doubtful whether the above effect is ascribed to the essential activity of catalyst against stereoregulation or to the content of catalyst species available for stereoregulation.

III. ZIEGLER-TYPE CATALYST

Ziegler-type catalyst is too complicated to be discussed here. On this catalyst tremendous work has been done by several authors and there are a large number of approaches to the mechanism of activation and stereoregulation. In this paper I will only refer to its correlation with our multi-center coordination mechanism.

Among many problems concerning Ziegler-Natta catalyst the followings seem to be noteworthy for stereoregulation, *i. e.*, stereoregulating ability of catalyst is depending upon both Lewis base component such as triethylaluminum and Lewis acid component such as titanium trichloride. Crystalline titanium chloride is most excellent as component and its crystal structure affects the content of crystalline polymer. There has been no paper reporting that soluble catalysts could afford crystalline polymer despite their excellent activity. These facts seem to favor the concept that the stereoregulating catalyst is not simple titanium chloride or related compound but complex compound consisting of both titanium compound and metal alkyl. The catalyst system would be considerably high molecular weight compound with crystalline or associated structure. Therefore, I decline the theories taking simple titanium tri- or dichloride as an actual active species for stereoregulation, although it is permitted to have the ability of inducing non-regular polymerization. On the other hand, many authors proposed the complex compounds consisting of titanium trichloride and metal alkyl, which are linked by half-bonding or by coordination such that,



This type of structure is similar to that I propose hitherto for catalyst of stereoregular polymerization. However, actual Ziegler-Natta catalyst is to be more complicated one, because the above type of complex is found also in soluble catalyst of dicyclopentadienyltitanium dichloride—triethylaluminum, which affords merely atactic polymer. And the effect of crystallinity of titanium trichloride on stereoregulating ability in polymerization is difficult to explain by the above complex. But if the complex is assumed to occur on a special surface of titanium trichloride crystal by chemisorption of trialkylaluminum, the above fact may easily be explained. Fig. 17 is one of possible examples.

Here, the special position such as edge of crystal may be available for suitable place. The array of alkylmetal adsorbed on edge affords the suitable places capable of coordinating with monomer as well as anionic chain end. According to this

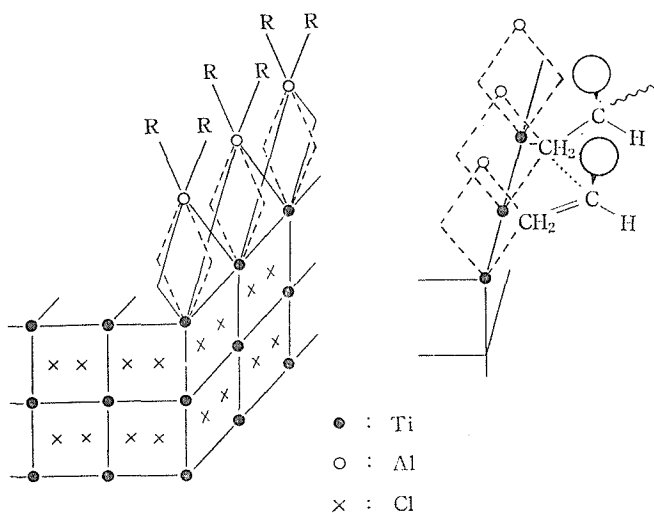


Fig. 17.

model the stereoregulation may be possible from the steric requirement of methyl group toward ligand on alkylmetal or toward crystall wall. Trialkylaluminum is regarded both as initiator and as terminator for polymerization²²⁾ and this fact may be explained by the assumption that the complex has both active and inactive site for polymerization, for example, the site linked by half-bonding and that by normal bonding, respectively, which are illustrated as (A) and (B) in Fig. 18.

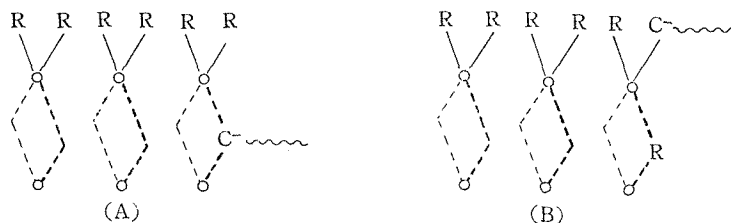
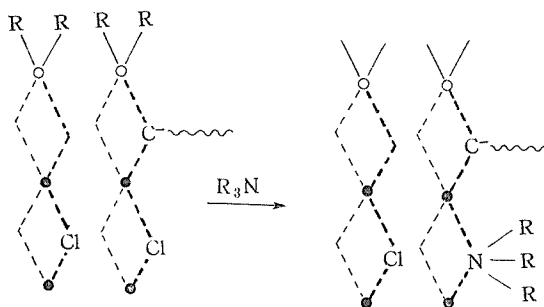
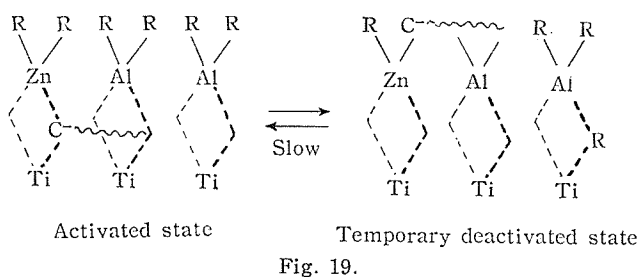


Fig. 18.

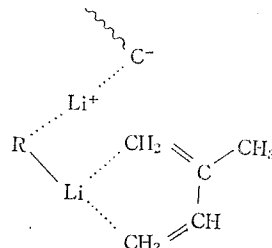
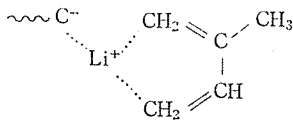
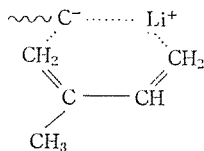
It was also reported that addition of dialkylzinc renders the depression of degree of polymerization without affecting the stereoregulation²³⁾ and addition²⁴⁾ of amine tends to enhance the stereoregulation. These facts seem to be explained also through this model with assumption that the chemisorption of diethylzinc takes place locally instead of trialkylaluminum and half-bonding resulted between zinc and titanium is less strong and therefore the temporary deactivation may be resulted by rearrangement of active polymer chain to inactive position (Fig. 19). Suitable explanation for effect of added amine will be possible by either the scavenging of undesirable material such as aluminum trichloride or the replacement of chlorine atom of titanium trichloride by bulky amine group (Fig. 20). This may be possible because the electronegativity of nitrogen is very close to that of chlorine.



IV. CIS AND TRANS POLYMERIZATION OF DIOLEFIN

There are two types of addition for conjugated diolefin, *i. e.*, 1,4- and 1,2(or 3,4-) additions. Stereochemically 1,4-polymer is classified into *cis*- and *trans*-forms and 1,2-polymer into *syndio*- and *iso*-tactic configurations. *Cis*-polyisoprene and *cis*-polybutadiene are very important from industrial view-point. They are successfully prepared by use of lithium catalyst or modified Ziegler catalyst but they are not the same in catalytic selectivity. Lithium or alkyl lithium is known to be suitable for *cis*-polymerization of isoprene but not for butadiene, the latter of which has been reported to be successful by use of modified Ziegler type catalyst containing cobalt or nickel salt or titanium iodide as component in contrast to undesired result in isoprene.

In the case of diolefin stereoregulation is concerned with the reaction form of monomer in itself. Stearns²⁵⁾ proposed cyclic mechanism for monomer conformation for accounting for lithium-catalyzed *cis*-polymerization of isoprene (Fig. 21). But he did not elucidate the reason why butadiene did not afford *cis*-polymer. I rather prefer the mechanism through two-point coordination with respect to monomer as shown in Figs. 22 and 23.



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Modified Ziegler catalyst is available for cis-polymerization of butadiene, whereby iron group such as iron, cobalt and nickel halide or related compounds are used and this fact agrees dimensionally with the complex formation of the above type as indicated in Fig. 24.

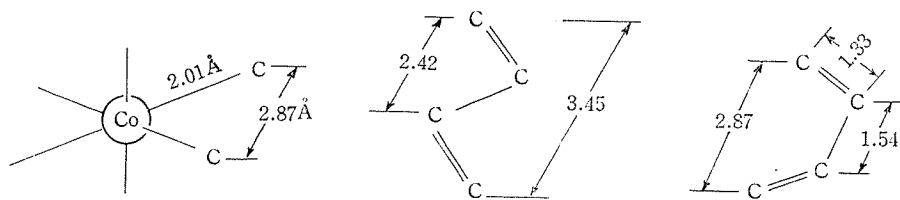


Fig. 24.

Table 10 illustrates the lengths of metal—carbon bond and the distances between two carbons adjacent to each other.

Table 10.

Metal	Radius of metal (Å)	Length of metal-carbon bond (Å) ^{a)}	Distance between carbon-carbon (Å) ^{b)}
Cu	1.28	2.05	2.90
Zn	1.38	2.15	3.04
Ti	1.45	2.22	3.15
V	1.36	2.13	3.01
Cr	1.28	2.05	2.90
Mn	1.31	2.08	2.94
Fe	1.27	2.04	2.88
Co	1.26	2.03	2.87
Ni	1.24	2.01	2.84
Li	1.57	2.34	2.34 ^{c)}

^{a)} Radius of carbon is estimated to be 0.77 Å.

^{b)} Bond angle is estimated to be 90°.

^{c)} Bond angle is estimated to be 60° for <Li-C-Li of halfbonded complex.

The table shows that only cobalt, nickel and iron have suitable carbon—carbon distance for coordination, when 1,4-distance of cis-diolefin is estimated to be 2.78 Å.

From Pauling's concept of electronegativity the bond length is closely correlated to the electronegativities of metal and linked atom and it is much shortened in polar bond. For the same reason, metal linked with hetero-atoms of large electronegativity has partial positive charge and therefore the length of carbon-metal bond to be formed by further coordination is shortened according to the ionicity (charge density) of metal.

Based on this assumption, the charge density of metal halides are calculated as listed in Table 11, where it is concluded that metals having moderate charge density, *e. g.*, titanium iodide, nickel or cobalt chloride seem to be suitable for cis-addition, whereas strongly polarized metal salts, *e. g.*, titanium and vanadium chloride etc., indicate rather 1,2- or trans-addition. For isoprene the suitable

Table 11. Charge density on catalyst component.

Catalyst component	Charge density	Butadiene	Isoprene
TiI ₄	0.22	Cis (86%)	—
NiCl ₂	0.30	Cis (97%)	Poorly active
CoCl ₂	0.30	Cis (87%)	Poorly active
TiBr ₄	0.34	Cis (75%)	Poorly active
CrCl ₃	0.39	1, 2	Inactive
TiCl ₄	0.42	Trans	Cis (>95%)
RLi	0.42	Trans and cis	Cis (>95%)
MnCl ₃	0.42	1, 2	1, 2
RNa	0.47	1, 2	1, 2 and 3, 4
Ti(OBu) ₄	0.63	Trans	—
VCl ₃	0.39	Trans	Trans

ionicity of metal seems to lie in stronger region and titanium iodide is too weak for polymerization. Steric hindrance of methyl group in isoprene may require larger positive charge of catalyst metal for coordination. Fig. 25 shows one set of hypothetical models accounting for cis and other polymerization, where it is assumed that as the distance between two neighboring positions for coordination becomes small, the structure becomes favorable for cis-, trans- and 1,2-addition according to the order, whose suitable distances are estimated at 2.87 Å (cis), 2.42 Å (1,3 distance for trans form) and less than 2.42 Å (1,2-addition), respectively. Here a complex catalyst having two coordination centers, *i. e.*, metal alkyl—metal salt combination, which dissociates ionically to induce anionic polymerization and

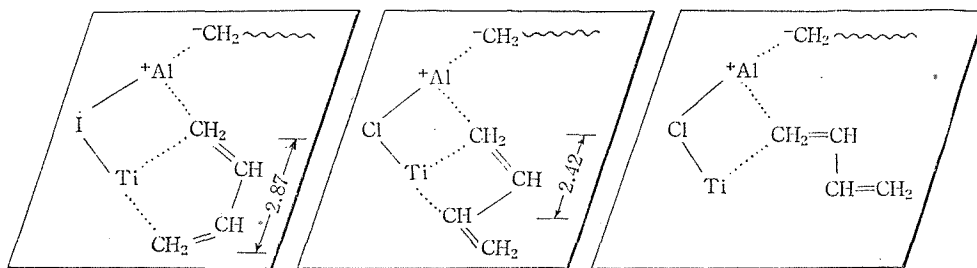


Fig. 25.

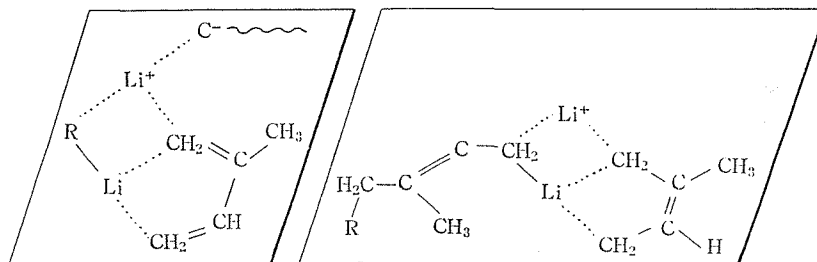


Fig. 26.

Fig. 27.

the counter cation combined with metal salt may play stereospecific regulation of monomer coordinated with metal salt component. Single cation does not explain stereoregulation and Lewis acid alone does not initiate anionic polymerization. Cis-addition of isoprene may be accounted for by assuming the associated form of alkyl lithium or isoprene-alkyl lithium adduct (Figs. 26 and 27).

CONCLUSION

In this article it is emphasized that the catalysts having two coordination centers would be favorable for stereoregulation; one center is counter ion and the other center is linked with ion by half-bonding, oxide linkage and ion-molecule linking through coordination. The first center is paired with polymer chain end by forming ion pair and the second center regulates free rotation in chain end by coordination with two adjacent polar substituents for polymerization of vinyl compounds. In the case where the key atom is present in monomer such as aldehyde, alkylene oxide, α -olefin and diolefin, one or two positions of monomer are linked with two coordination centers of catalyst, whereby stereoregulation can be effectuated by the ligand of catalyst. Finally, cis-addition in diolefin is explained by suitable 1,4-coordination with catalyst center. Of course, the stereoregulation in polymerization is so complicated that inquisitive discussion without further experiments is rather harmful, but the so-called multi-center coordination concept seems often to be helpful for consideration of stereoregulation.

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